John E. McMurry • Robert C. Fay

General Chemistry: Atoms First

Chapter 20
Transition Elements and Coordination Chemistry

Lecture Notes

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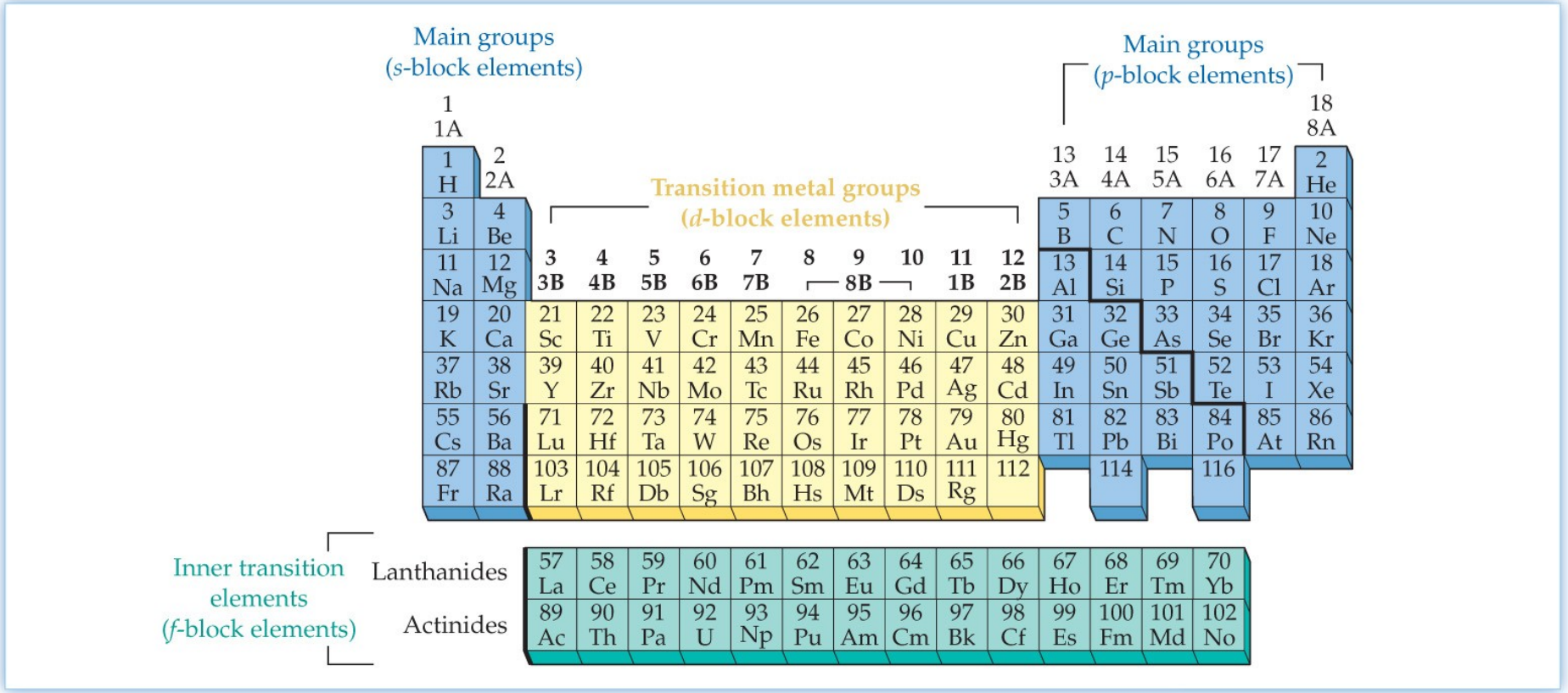
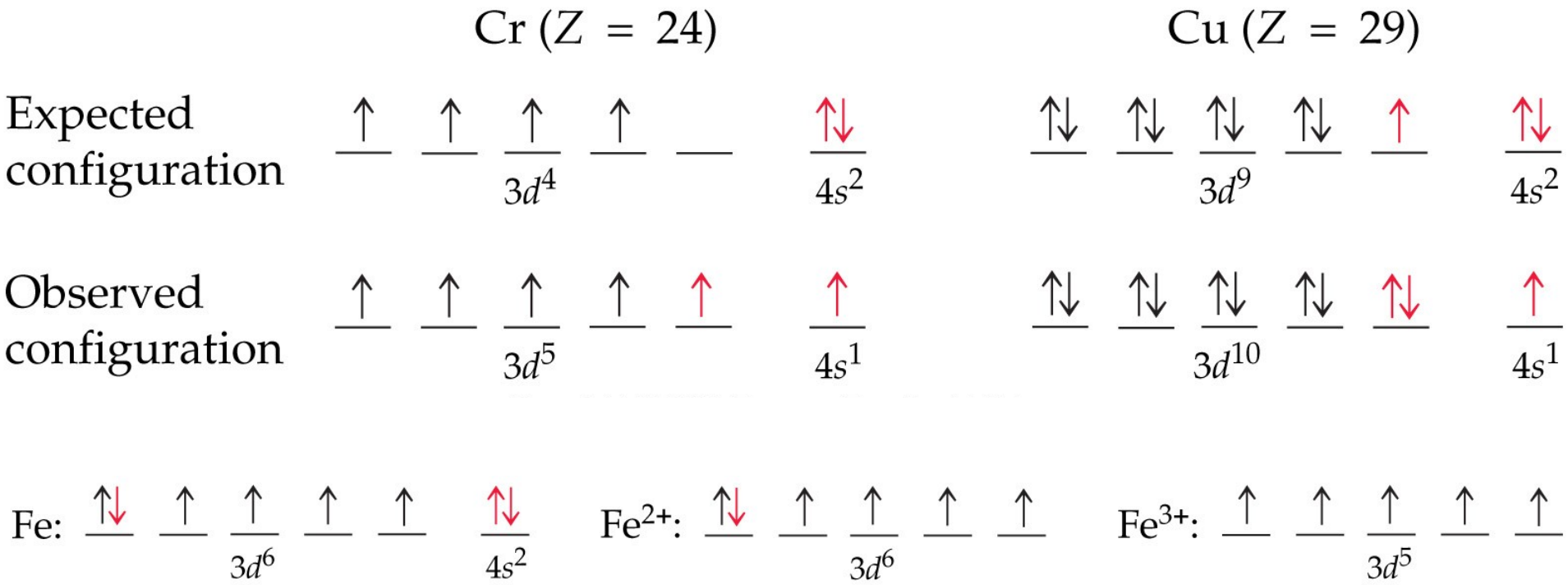
Electron Configurations



Electron Configurations

Sc ($Z = 21$): [Ar] $3d^1\ 4s^2$ ⟶ **Zn** ($Z = 30$): [Ar] $3d^{10}\ 4s^2$



Electron Configurations

TABLE 20.1 Selected Properties of First-Series Transition Elements

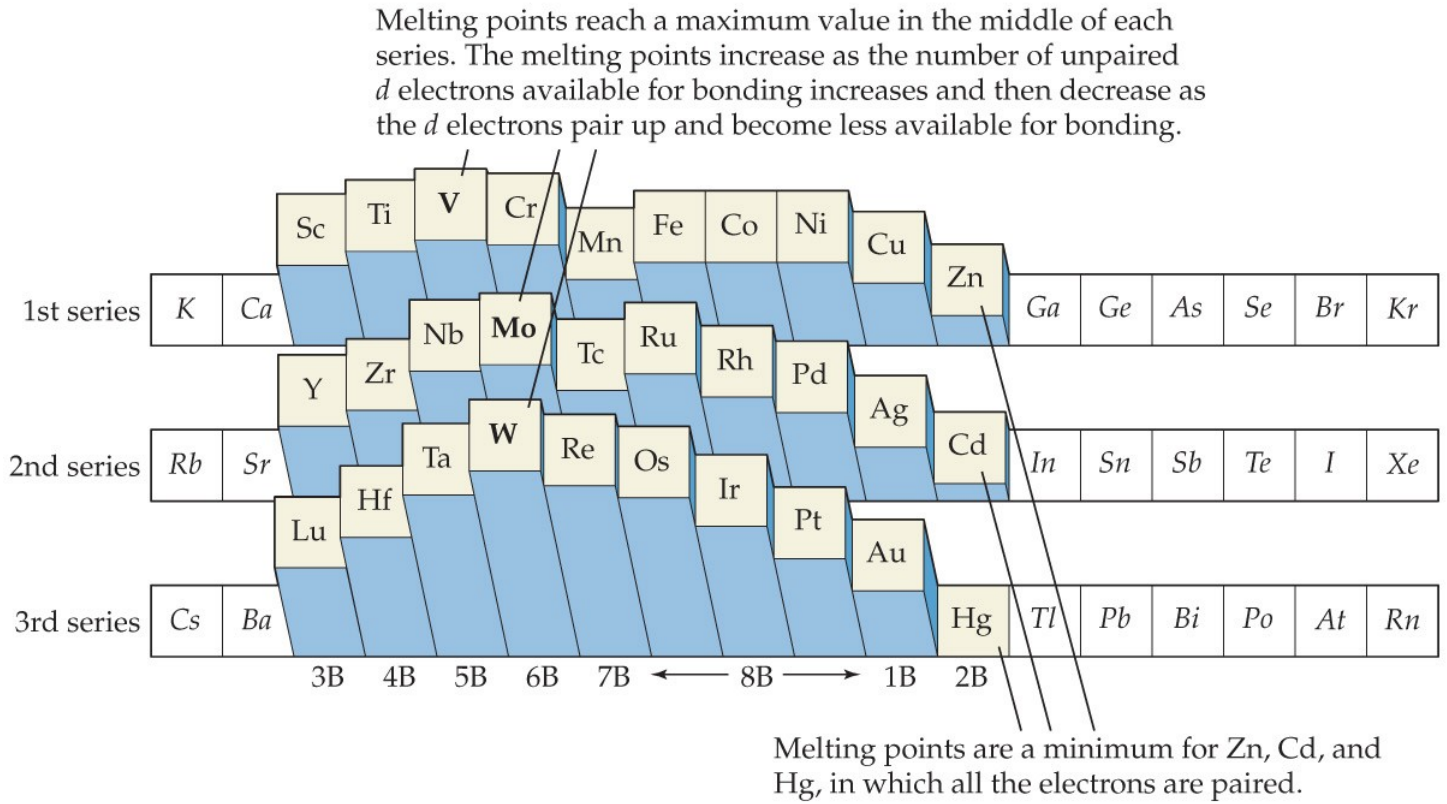
Group:	3B	4B	5B	6B	7B	8B			1B	2B
Element:	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Valence electron configuration										
M atom	$3d^1\,4s^2$	$3d^2\,4s^2$	$3d^3\,4s^2$	$3d^5\,4s^1$	$3d^5\,4s^2$	$3d^6\,4s^2$	$3d^7\,4s^2$	$3d^8\,4s^2$	$3d^{10}\,4s^1$	$3d^{10}\,4s^2$
M^{2+} ion		$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$	$3d^{10}$
M^{3+} ion	$3d^0$	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$			
Elec. Conductivity*	3	4	8	11	1	17	24	24	96	27
Melting point (°C)	1541	1668	1910	1907	1246	1538	1495	1455	1085	420
Boiling point (°C)	2836	3287	3407	2671	2061	2861	2927	2913	2562	907
Density (g/cm^3)	2.99	4.51	6.0	7.15	7.3	7.87	8.86	8.90	8.96	7.13
Atomic radius (pm)	162	147	134	128	127	126	125	124	128	134
E_i (kJ/mol)†										
First	633	659	651	653	717	762	760	737	745	906
Second	1235	1310	1410	1591	1509	1562	1648	1753	1958	1733
Third	2389	2653	2828	2987	3248	2957	3232	3395	3555	3833

*Electrical conductivity relative to an arbitrary value of 100 for silver

†Ionization energy

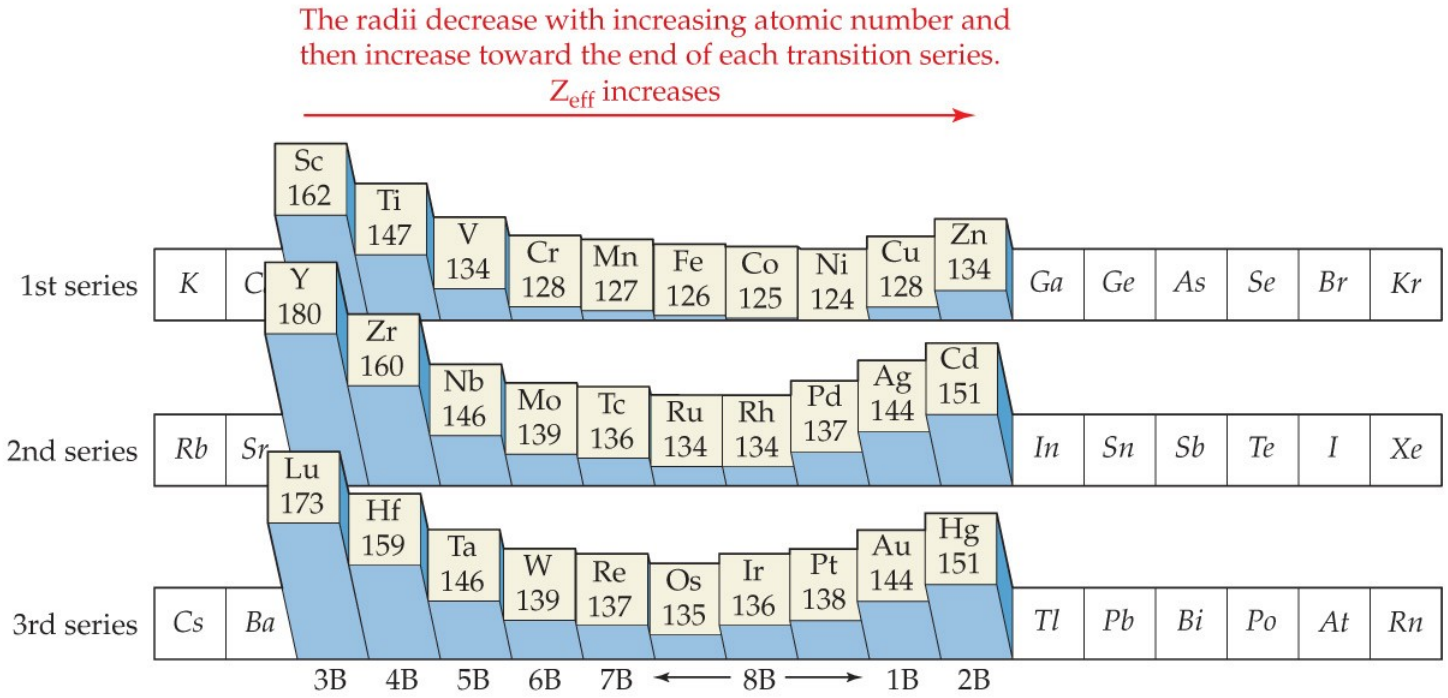
Properties of Transition Elements

Metallic Properties



Properties of Transition Elements

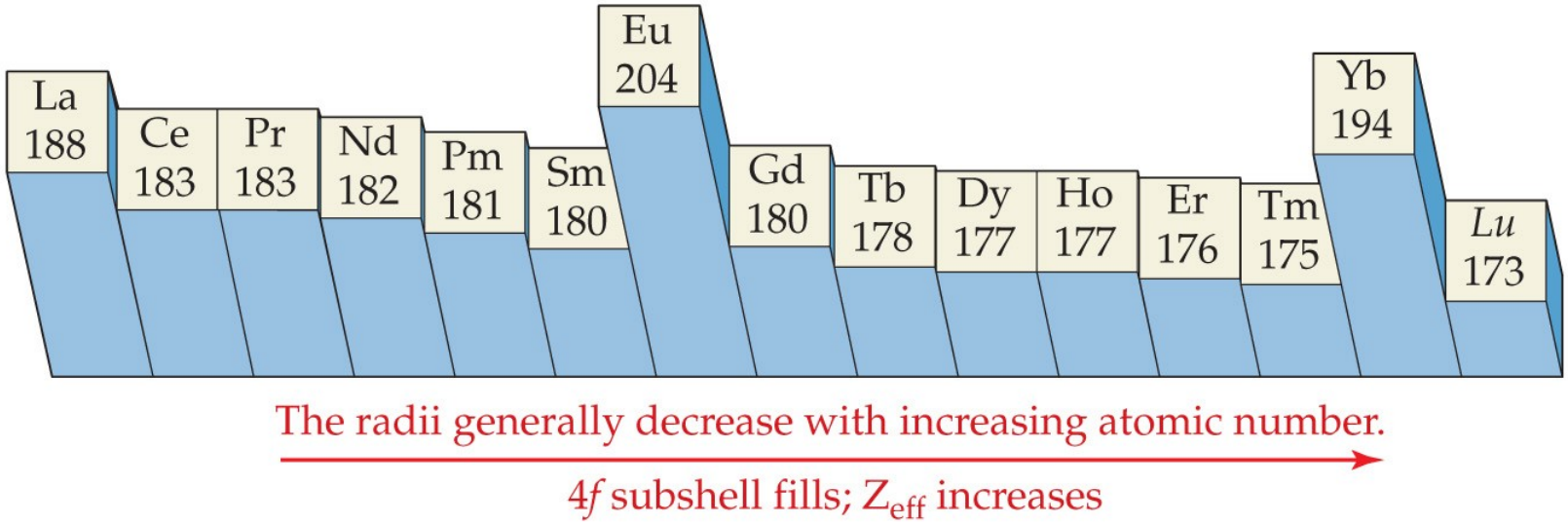
Atomic Radii



The second- and third-series transition elements have nearly identical radii.

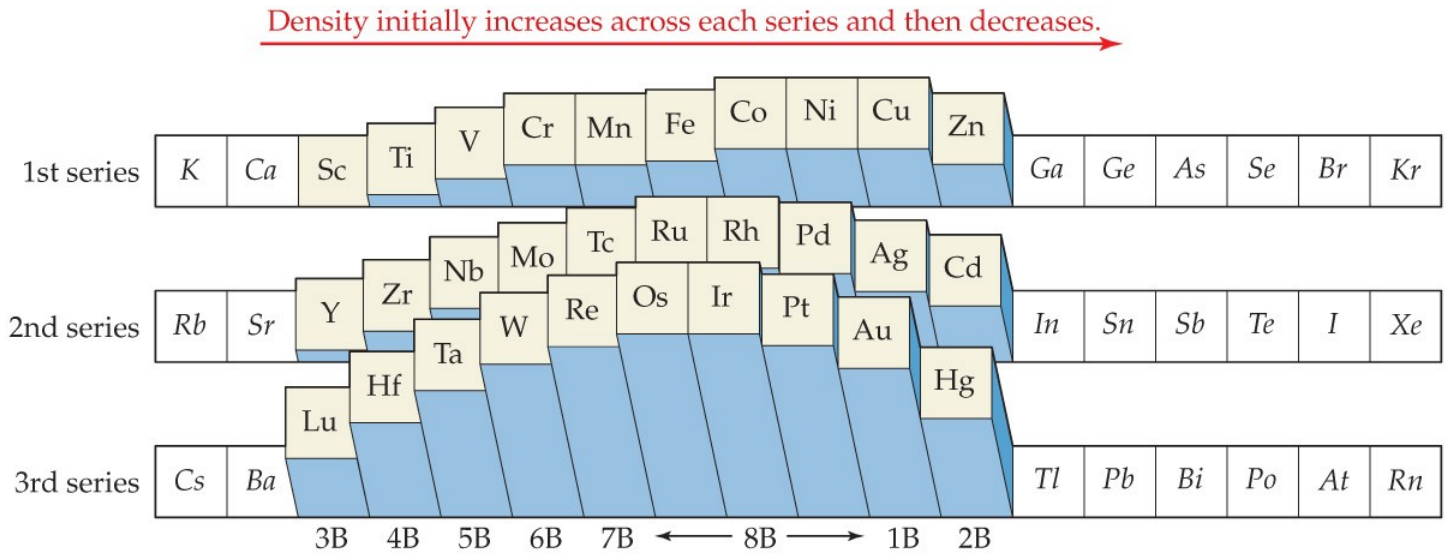
Properties of Transition Elements

Atomic Radii



Properties of Transition Elements

Atomic Densities



Properties of Transition Elements

Ionization Energies and Oxidation Potentials

TABLE 20.2 Standard Potentials for Oxidation of First-Series Transition Metals

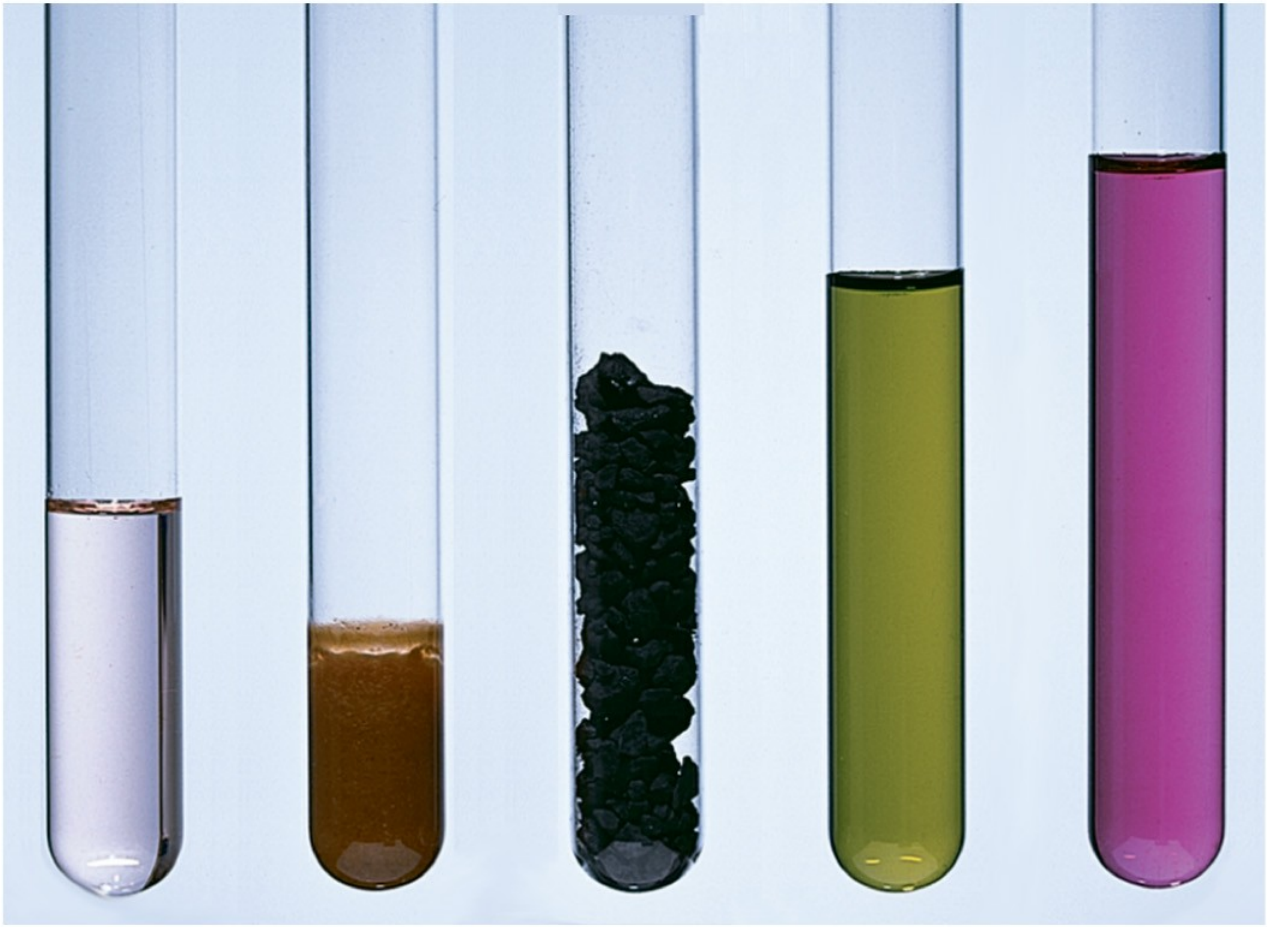
Oxidation Half-Reaction	$E°$ (V)	Oxidation Half-Reaction	$E°$ (V)
$Sc(s) \longrightarrow Sc^{3+}(aq) + 3\,e^-$	2.08	$Fe(s) \longrightarrow Fe^{2+}(aq) + 2\,e^-$	0.45
$Ti(s) \longrightarrow Ti^{2+}(aq) + 2\,e^-$	1.63	$Co(s) \longrightarrow Co^{2+}(aq) + 2\,e^-$	0.28
$V(s) \longrightarrow V^{2+}(aq) + 2\,e^-$	1.18	$Ni(s) \longrightarrow Ni^{2+}(aq) + 2\,e^-$	0.26
$Cr(s) \longrightarrow Cr^{2+}(aq) + 2\,e^-$	0.91	$Cu(s) \longrightarrow Cu^{2+}(aq) + 2\,e^-$	−0.34
$Mn(s) \longrightarrow Mn^{2+}(aq) + 2\,e^-$	1.18	$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$	0.76

All but copper are positive.

$$M(s) + 2H^{1+}(aq) \longrightarrow M^{2+}(aq) + H_2(g) \qquad E° > 0\ V$$

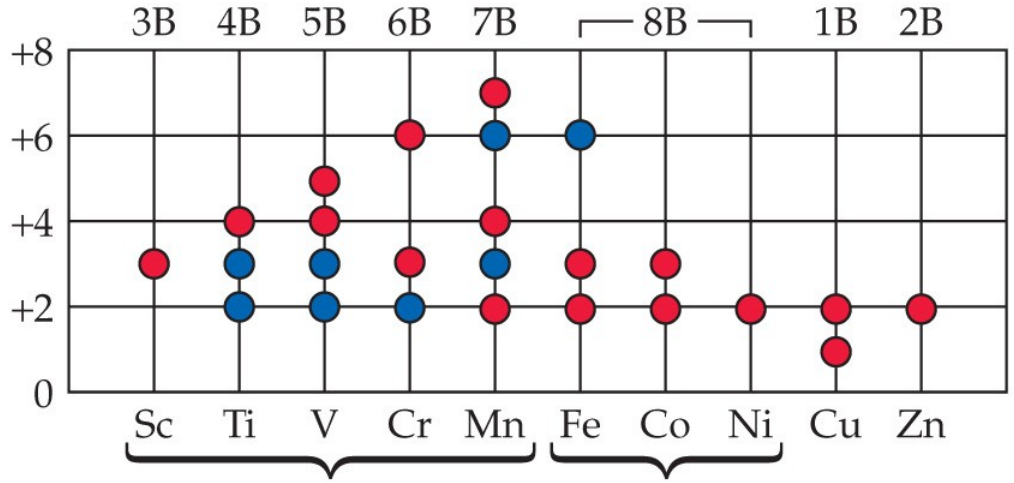
Copper requires a stronger oxidizing agent than HCl, such as HNO_3.

Oxidation States of Transition Elements



Manganese species:	$Mn^{2+}(aq)$	$Mn(OH)_3(s)$	$MnO_2(s)$	$MnO_4^{2-}(aq)$	$MnO_4^{-}(aq)$
Oxidation state of manganese:	+2	+3	+4	+6	+7

Oxidation States of Transition Elements



The highest oxidation state for the group 3B–7B metals is their periodic group number...

...but the group 8B transition metals have a maximum oxidation state less than their group number.

Oxidation States of Transition Elements

For group 8b, the loss or sharing of all the valence electrons is energetically prohibitive because of the increasing value of Z_{eff}. Consequently, only lower oxidation states are accessible. Also, they can sometimes be reduced to even lower oxidation states:

$$4Co^{3+}(aq) + 2H_2O(l) \longrightarrow 4Co^{2+}(aq) + O_2(g) + 4H^{1+}(aq)$$

$$E° = +0.58\ V$$

Chemistry of Selected Transition Elements

Chromium

- Chromium can be obtained by the reduction of the ore chromite ($FeCr_2O_4$) with carbon:

$$FeCr_2O_4(s) + 4C(s) \longrightarrow \underbrace{Fe(s) + 2Cr(s)}_{\text{Ferrochrome}} + 4CO(g)$$

Up to 30% Cr

- Pure chromium is obtained by reducing Cr_2O_3 with Al:

$$Cr_2O_3(s) + 2Al(s) \longrightarrow 2Cr(s) + Al_2O_3(s)$$

Chemistry of Selected Transition Elements

TABLE 20.3 Chromium Species in Common Oxidation States

	Oxidation State		
	+2	+3	+6
Acidic solution:	$Cr^{2+}(aq)$ Chromium(II) ion (Chromous ion) Blue	$Cr^{3+}(aq)$ Chromium(III) ion (Chromic ion) Violet	$Cr_2O_7^{2-}(aq)$ Dichromate ion Orange
Basic solution:	$Cr(OH)_2(s)$ Light blue	$Cr(OH)_3(s)$ Pale green $Cr(OH)_4^-(aq)$ Chromite ion Deep green	$CrO_4^{2-}(aq)$ Chromate ion Yellow

+0.41 V → (between +2 and +3)

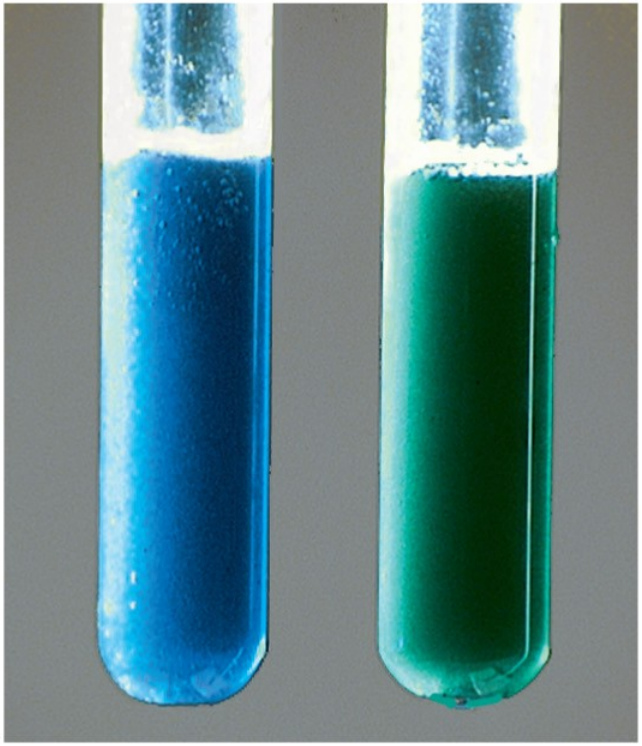
+1.36 V ← (between +3 and +6)

−0.13 V ← (between +3 and +6)

Chemistry of Selected Transition Elements

Chromium

Reaction of chromium metal with 6 M H_2SO_4 in the *absence* of air gives bubbles of H_2 gas and a solution containing the blue chromium(II) ion.



(a) (b)

Reaction of chromium metal with 6 M HCl in the *presence* of air yields a green solution containing chromium(III) species.

Chemistry of Selected Transition Elements

Chromium

- In basic solution, Cr^{3+} precipitates as $Cr(OH)_3$, a pale green solid which is amphoteric:

$$Cr(OH)_3(s) + 3H_3O^{1+}(l) \rightleftharpoons Cr^{3+}(aq) + 6H_2O(l)$$

$$Cr(OH)_3(s) + OH^{1-}(aq) \rightleftharpoons Cr(OH)_4{}^{1-}(aq)$$

Chemistry of Selected Transition Elements

Chromium

Slow addition of aqueous NaOH to a solution of the violet $Cr(H_2O)_6^{3+}$ ion…

…gives a pale green precipitate of chromium(III) hydroxide, $Cr(OH)_3$.

The $Cr(OH)_3$ dissolves on addition of H_2SO_4 …

…re-forming the $Cr(H_2O)_6^{3+}$ ion.

$Cr(OH)_3$ also dissolves on addition of excess NaOH…

…yielding the deep green chromite ion, $Cr(OH)_4^-$.

Chemistry of Selected Transition Elements

Chromium

- In the +6 oxidation state, the most important solution species are yellow chromate ion and the orange dichromate ion:

$$2CrO_4^{2-}(aq) + 2H^{1+}(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$

yellow orange

- The orange dichromate ion is a powerful oxidizing agent in acidic solution and is widely used as an oxidant in analytical chemistry:

$$Cr_2O_7^{2-}(aq) + 14H^{1+}(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

$$E° = +1.36\ V$$

Chemistry of Selected Transition Elements

$$2\,CrO_4^{2-}(aq) + 2\,H^+(aq) \longrightarrow Cr_2O_7^{2-}(aq) + H_2O(l)$$

An aqueous solution of sodium chromate (Na_2CrO_4).

On addition of dilute sulfuric acid to a sodium chromate solution, the yellow CrO_4^{2-} ion is converted to the orange $Cr_2O_7^{2-}$ ion.

Chemistry of Selected Transition Elements

Iron

- In the *absence* of air, iron metal will react with acids:

$$Fe(s) + 2H^{1+}(aq) \longrightarrow Fe^{2+}(aq) + H_2(g) \quad E° = +0.45\ V$$

spontaneous

$$Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^- \quad E° = -0.77\ V$$

nonspontaneous

- In the *presence* of air, Fe^{2+} is slowly oxidized:

$$4Fe^{2+}(aq) + O_2(g) + 4H^{1+}(aq) \longrightarrow 4Fe^{3+}(aq) + 2H_2O(l)$$

$E° = +0.46\ V$

spontaneous

Chemistry of Selected Transition Elements

Iron

- The red-brown colored $Fe(OH)_3$ will precipitate in basic solutions, but unlike the analogous $Cr(OH)_3$, it is not amphoteric (dissolves in base):

$$Fe^{3+}(aq) + 3OH^{1-}(aq) \longrightarrow Fe(OH)_3(s)$$

Chemistry of Selected Transition Elements

Copper

- Copper sulfides are separated from ores and then hot air is blown through molten copper(I) sulfide (Cu_2S):

$$Cu_2S(l) + O_2(g) \longrightarrow 2Cu(l) + SO_2(g)$$

- Over time, copper turns green due to oxidation:

$$2Cu(s) + O_2(g) + CO_2(g) + H_2O(g) \longrightarrow Cu_2(OH)_2CO_3(s)$$

$$Cu_2(OH)_2CO_3(s) + H_2SO_4(aq) \longrightarrow$$

$$Cu_2(OH)_2SO_4(s) + CO_2(g) + H_2O(l)$$

Green patina

Chemistry of Selected Transition Elements

Copper

Coordination Compounds

Coordination Compound: A compound in which a central metal ion or atom is attached to a group of surrounding molecules or ions by coordinate covalent bonds.

Ligands: The ions, molecules, or atoms that surround the central metal ion.

Ligand Donor Atom: The atoms in the ligand that bond to the central metal ion.

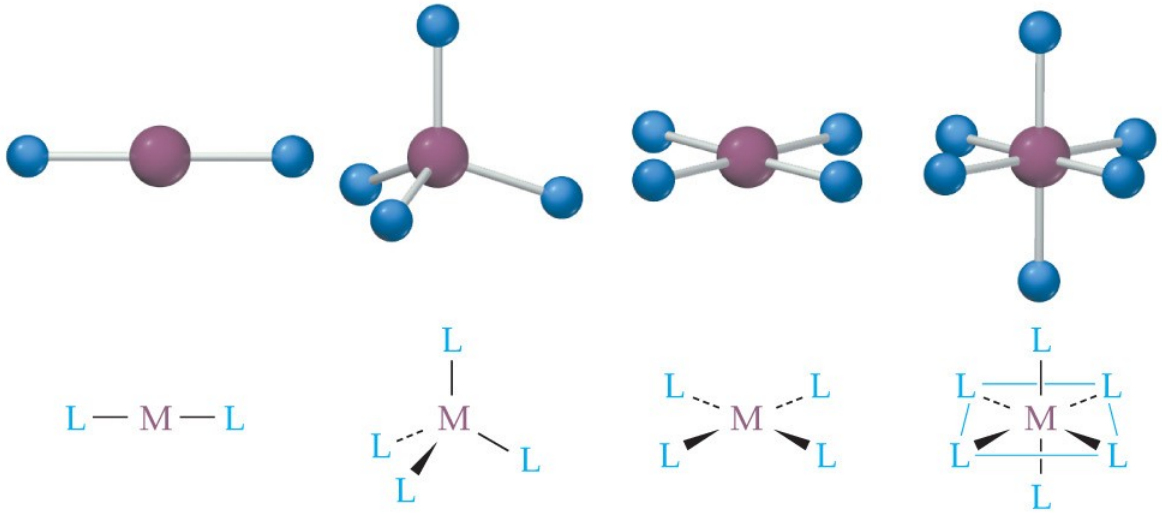
Coordination Number: The number of ligand donor atoms that surround a central metal ion.

Coordination Compounds

TABLE 20.4 Examples of Complexes with Various Coordination Numbers

Coordination Number	Complex
2	$[Ag(NH_3)_2]^+$, $[CuCl_2]^-$
3	$[HgI_3]^-$
4	$[Zn(NH_3)_4]^{2+}$, $[Ni(CN)_4]^{2-}$
5	$[Ni(CN)_5]^{3-}$, $Fe(CO)_5$
6	$[Cr(H_2O)_6]^{3+}$, $[Fe(CN)_6]^{3-}$
7	$[ZrF_7]^{3-}$
8	$[Mo(CN)_8]^{4-}$

Coordination Compounds



Linear (two-coordinate)

Tetrahedral (four-coordinate)

Square planar (four-coordinate)

Octahedral (six-coordinate)

In the octahedral arrangement, four ligands are at the corners of a square, with one more above and one below the plane of the square.

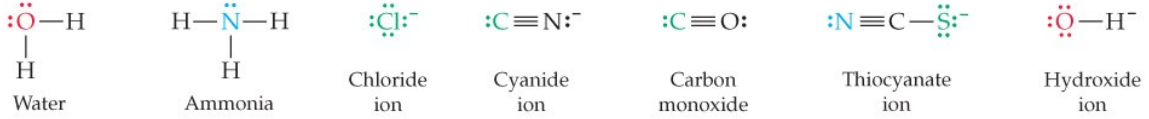
Ligands

Monodentate: One ligand donor atom that surrounds a central metal ion.

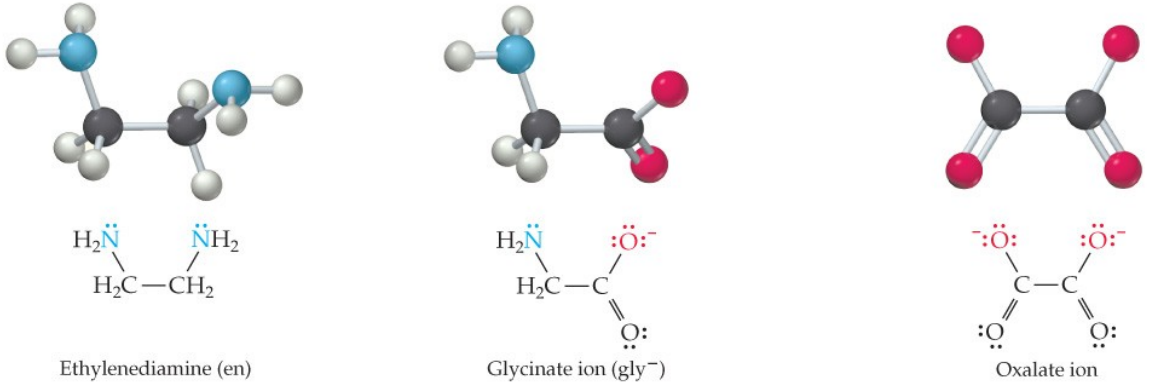
Polydentate: Two or more ligand donor atoms that surround a central metal ion.

Ligands

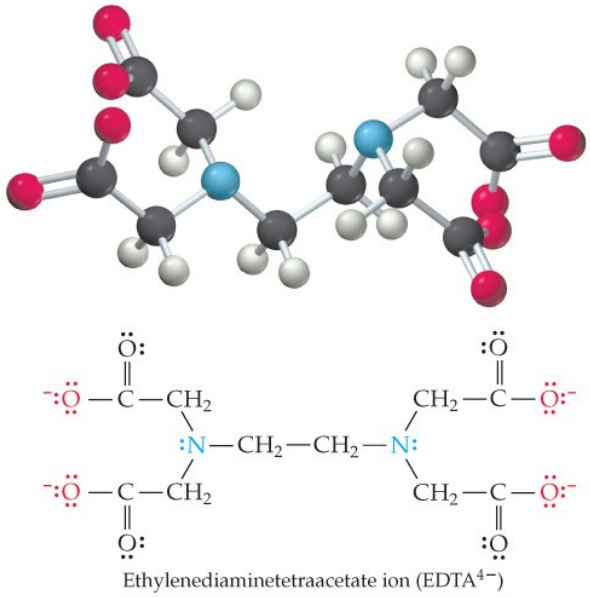
Monodentate ligands



Bidentate ligands

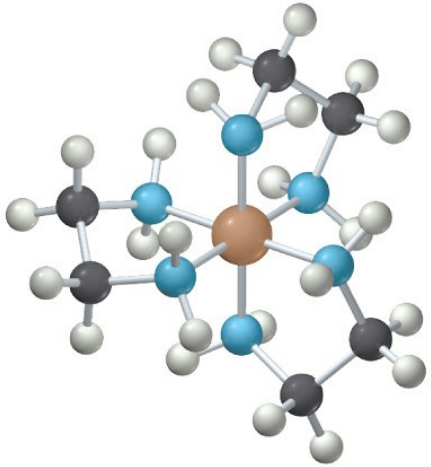


Hexadentate ligand

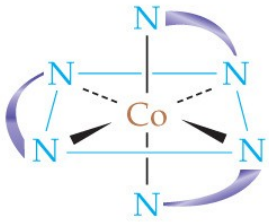


Ligands

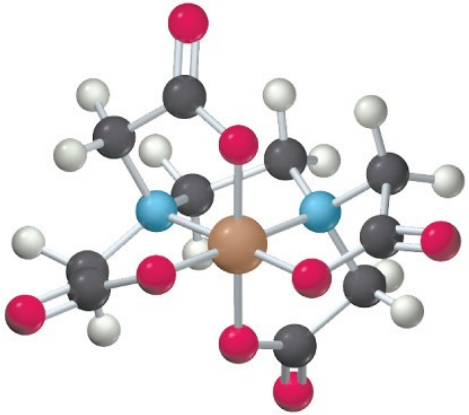
Chelating Agents: Polydentate ligands. Their multipoint attachment to a metal ion resembles the grasping of an object by the claws of a crab.



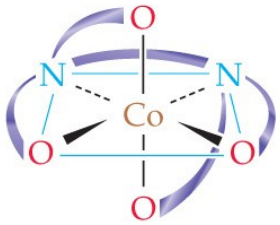
$[Co(en)_3]^{3+}$



Shorthand representation of the $[Co(en)_3]^{3+}$ ion. The complex contains three cobalt–ethylenediamine chelate rings. The symbol N⌒N represents a bidentate $NH_2CH_2CH_2NH_2$ ligand, which spans adjacent corners of the octahedron.

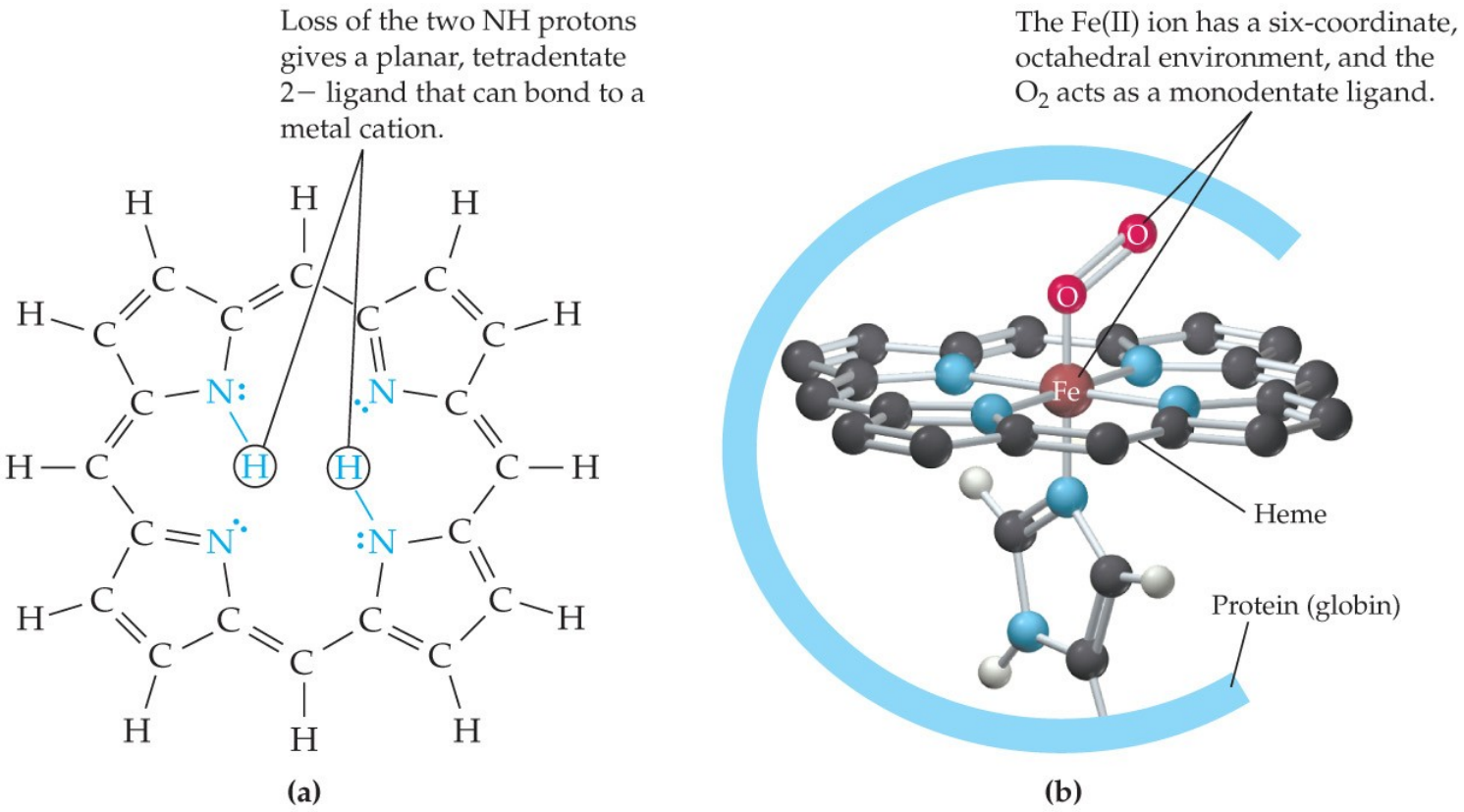


$[Co(EDTA)]^-$



Shorthand representation of the $[Co(EDTA)]^-$ ion. The hexadentate $EDTA^{4-}$ ligand uses its two N atoms and four O atoms to bond to the metal, thus forming five chelate rings.

Ligands


Loss of the two NH protons gives a planar, tetradentate 2− ligand that can bond to a metal cation.
(a)
The Fe(II) ion has a six-coordinate, octahedral environment, and the O_2 acts as a monodentate ligand.
Heme
Protein (globin)
(b)

Naming Coordination Compounds

1. If the compound is a salt, name the cation first and then the anion, just as in naming simple salts.

Naming Coordination Compounds

2. In naming a complex ion or a neutral complex, name the ligands first and then the metal. The names of anionic ligands end in *-o*. Neutral ligands are specified by their usual names except for H_2O, NH_3, and CO.

TABLE 20.5 Names of Some Common Ligands

Anionic Ligand	Ligand Name	Neutral Ligand	Ligand Name
Bromide, Br^-	Bromo	Ammonia, NH_3	Ammine
Carbonate, CO_3^{2-}	Carbonato	Water, H_2O	Aqua
Chloride, Cl^-	Chloro	Carbon monoxide, CO	Carbonyl
Cyanide, CN^-	Cyano	Ethylenediamine, en	Ethylenediamine
Fluoride, F^-	Fluoro		
Glycinate, gly^-	Glycinato		
Hydroxide, OH^-	Hydroxo		
Oxalate, $C_2O_4^{2-}$	Oxalato		
Thiocyanate, SCN^-	Thiocyanato* Isothiocyanato†		

*Ligand donor atom is S.
†Ligand donor atom is N.

Naming Coordination Compounds

3. If the complex contains more than one ligand of a particular type, indicate the number with the appropriate Greek prefix. The ligands are listed in alphabetical order, and the prefixes are ignored in determining the order.

4. If the name of a ligand itself contains a Greek prefix, then put the ligand name in parentheses and use one of the following alternative prefixes to specify the number of ligands: *bis-* (2), *tris-* (3), *tetrakis-* (4), and so forth.

5. Use a Roman numeral in parentheses immediately following the name of the metal to indicate the metal's oxidation state.

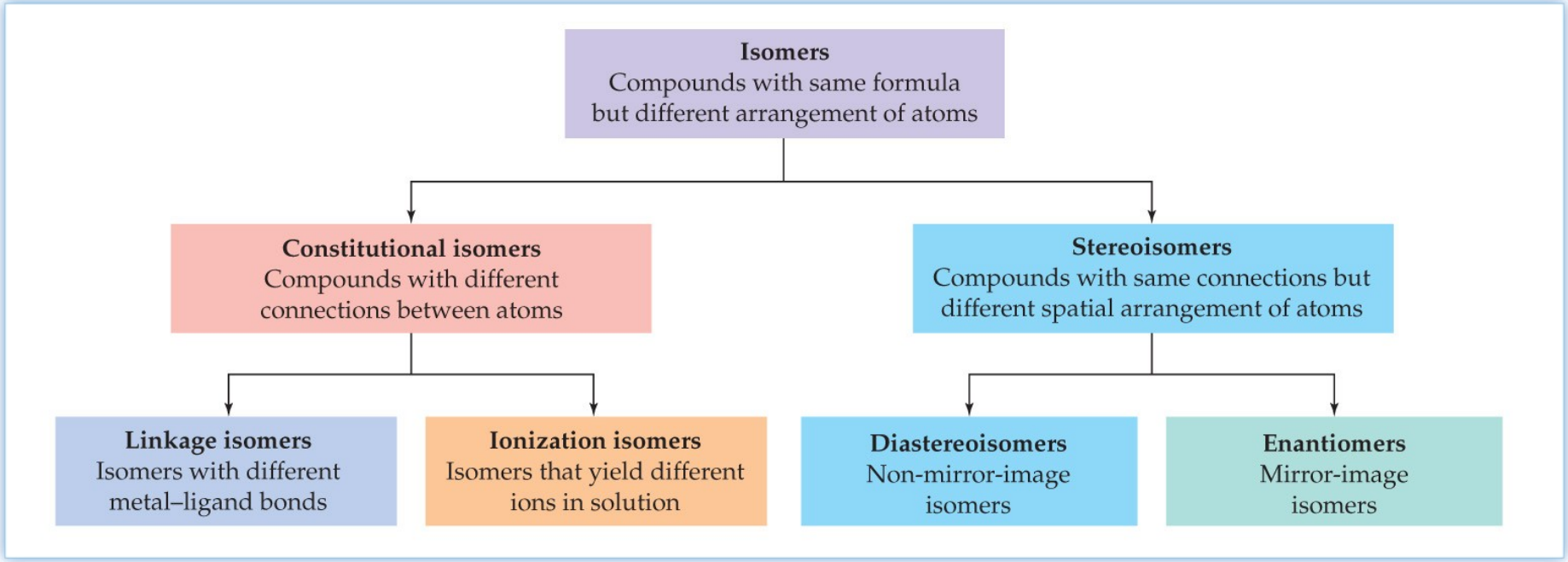
Naming Coordination Compounds

6. In naming the metal, use the ending *-ate* if the metal is an anionic complex. Some anion names are Latin.

TABLE 20.6 Names of Some Common Metallate Anions

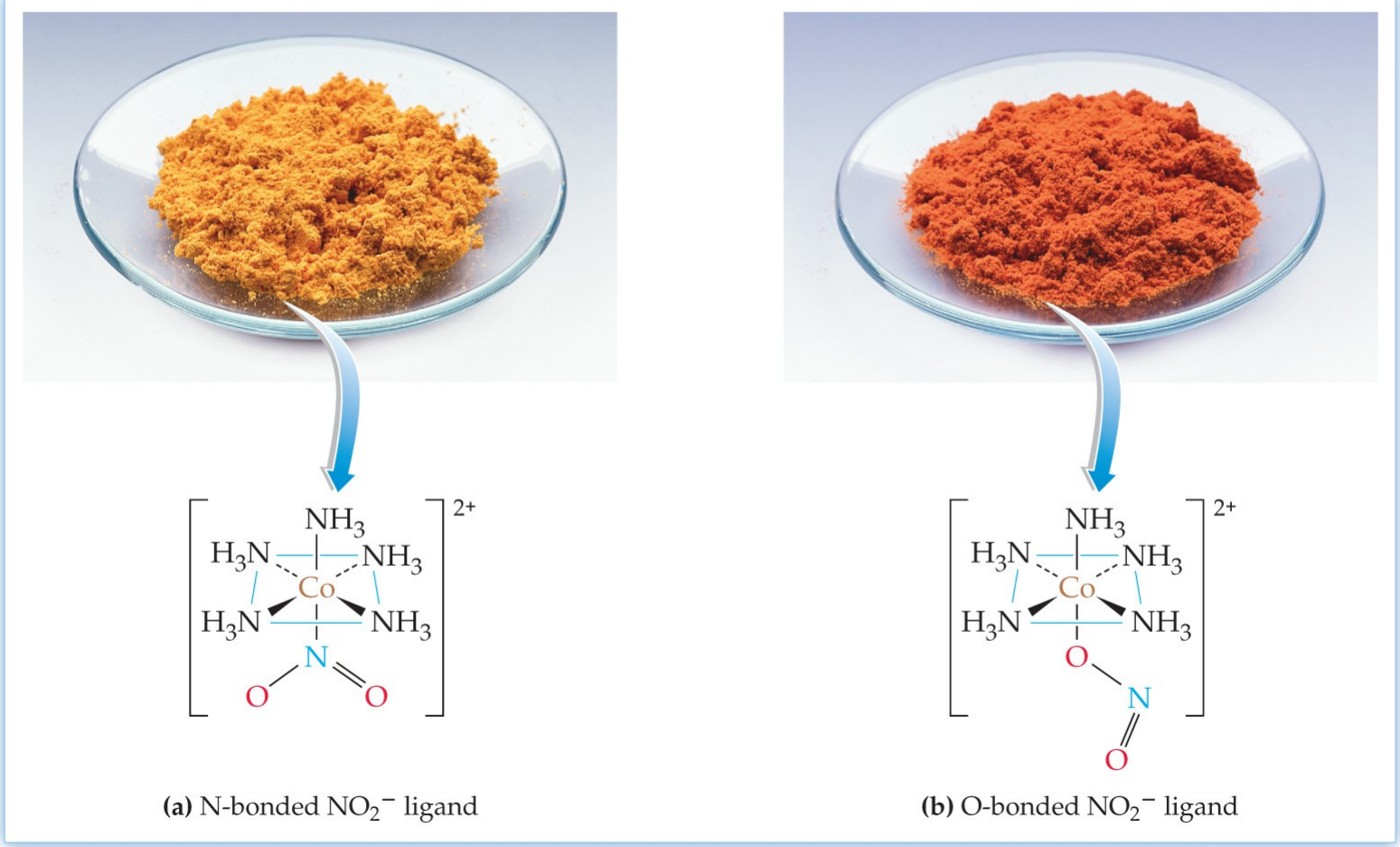
Metal	Anion Name	Metal	Anion Name
Aluminum	Aluminate	Iron	Ferrate
Chromium	Chromate	Manganese	Manganate
Cobalt	Cobaltate	Nickel	Nickelate
Copper	Cuprate	Platinum	Platinate
Gold	Aurate	Zinc	Zincate

Isomers


Isomers
Compounds with same formula but different arrangement of atoms
Constitutional isomers
Compounds with different connections between atoms
Stereoisomers
Compounds with same connections but different spatial arrangement of atoms
Linkage isomers
Isomers with different metal–ligand bonds
Ionization isomers
Isomers that yield different ions in solution
Diastereoisomers
Non-mirror-image isomers
Enantiomers
Mirror-image isomers

Isomers

Constitutional Isomers-Linkage Isomers



(a) N-bonded NO_2^- ligand

(b) O-bonded NO_2^- ligand

Isomers

Constitutional Isomers-Ionization Isomers

$[Co(NH_3)_5Br]SO_4$ A free sulfate ion.

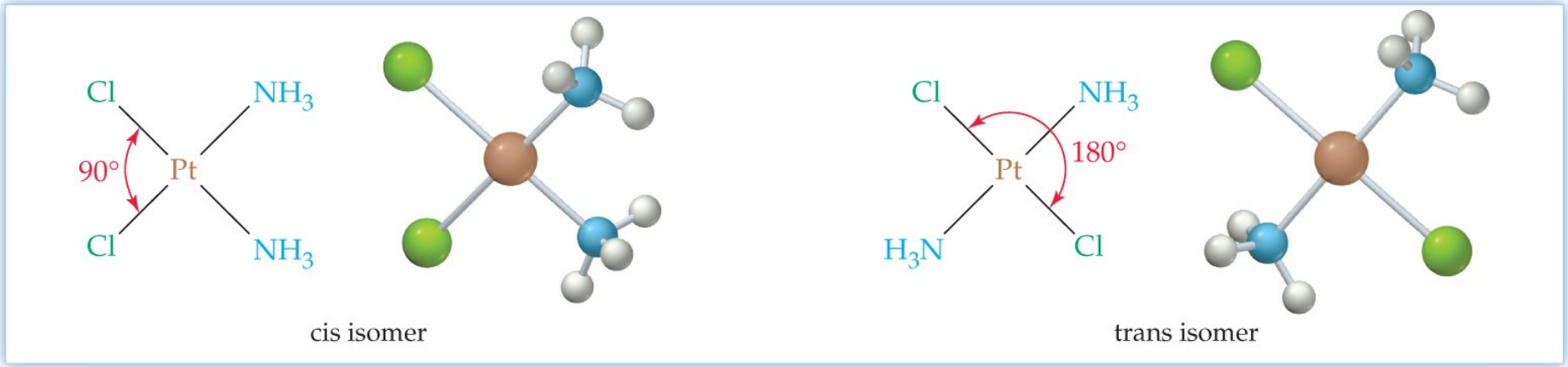
$[Co(NH_3)_5SO_4]Br$ A free bromide ion.

Isomers

Stereoisomers-Diastereoisomers

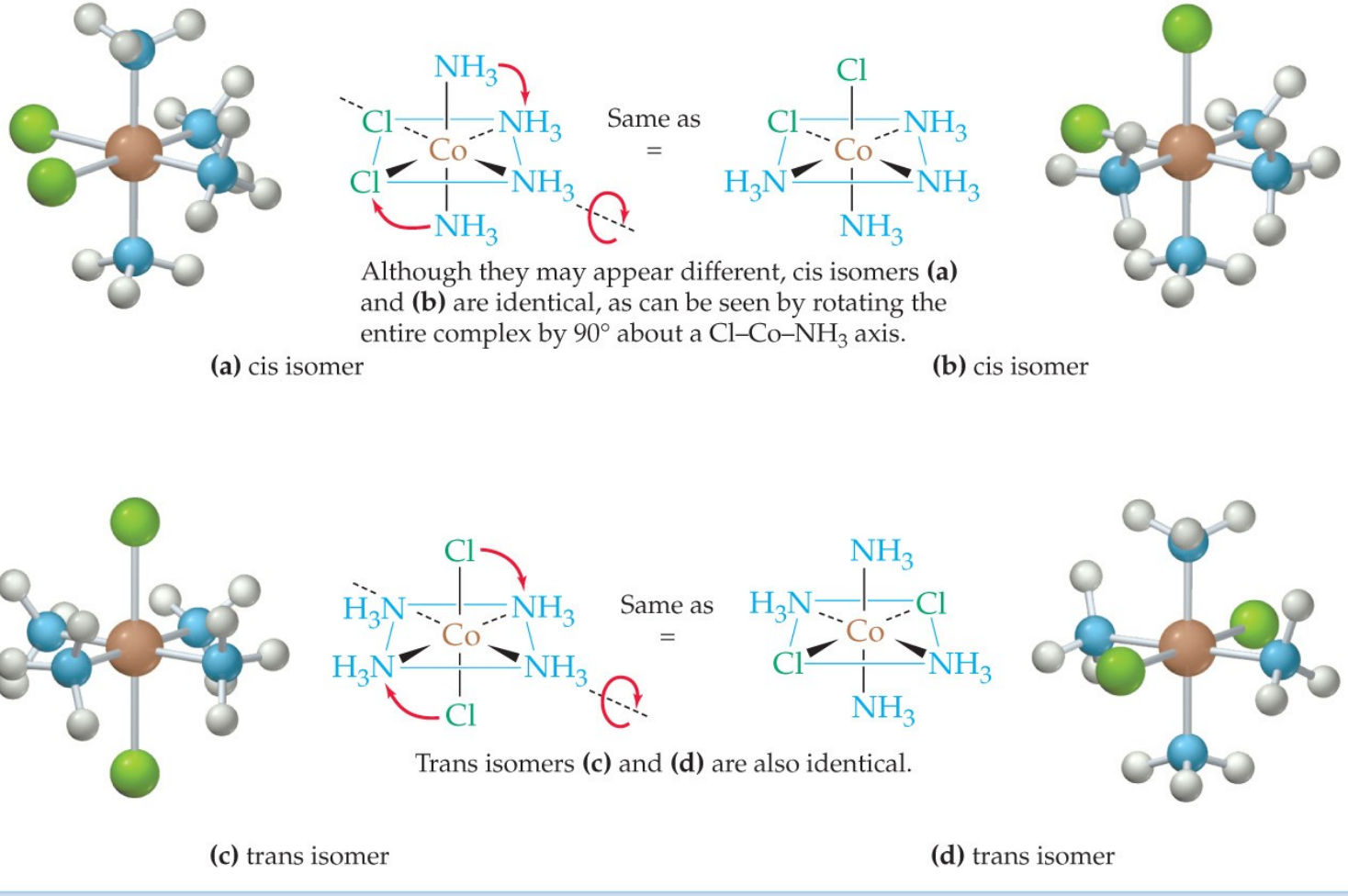
adjacent

opposite



Isomers

Stereoisomers-Diastereoisomers

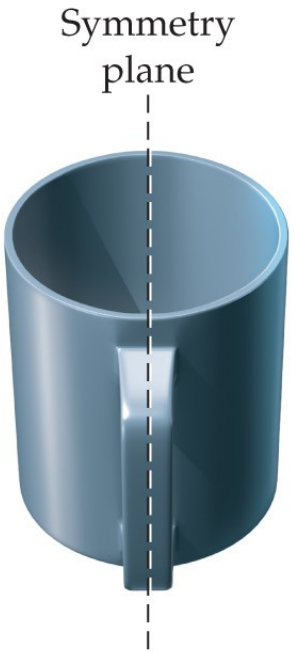


Enantiomers and Molecular Handedness

Chiral: Objects that have a handedness to them. Nonidentical mirror images.

Nonchiral: Objects that lack a handedness to them.

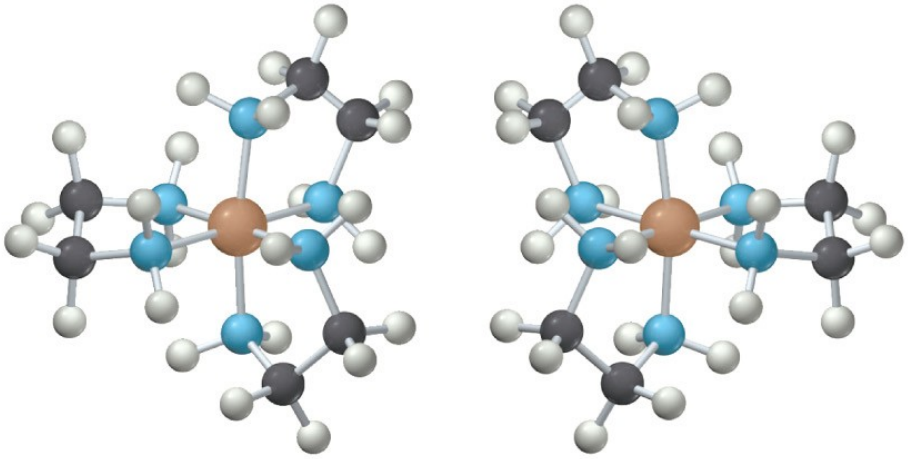
Enantiomers and Molecular Handedness

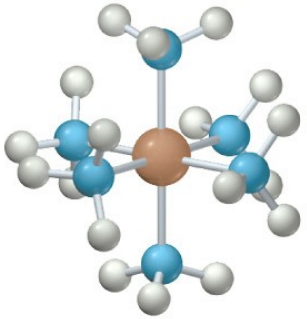


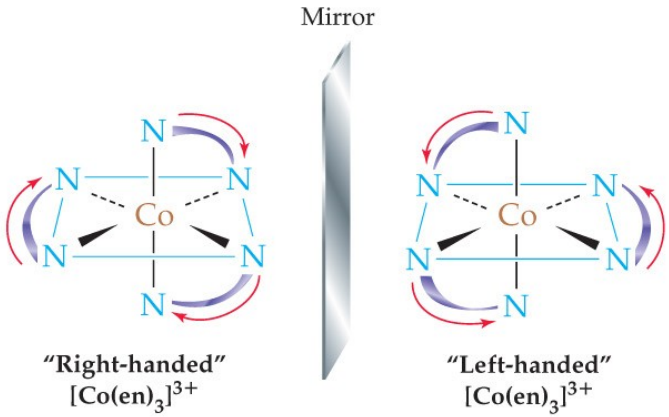
An achiral object like the coffee mug has a symmetry plane passing through it, making the two halves mirror images.

A chiral object like the hand has no symmetry plane because the two halves of the hand are not mirror images.

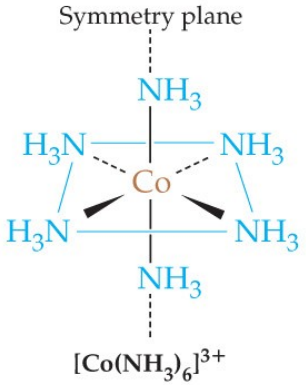
Enantiomers and Molecular





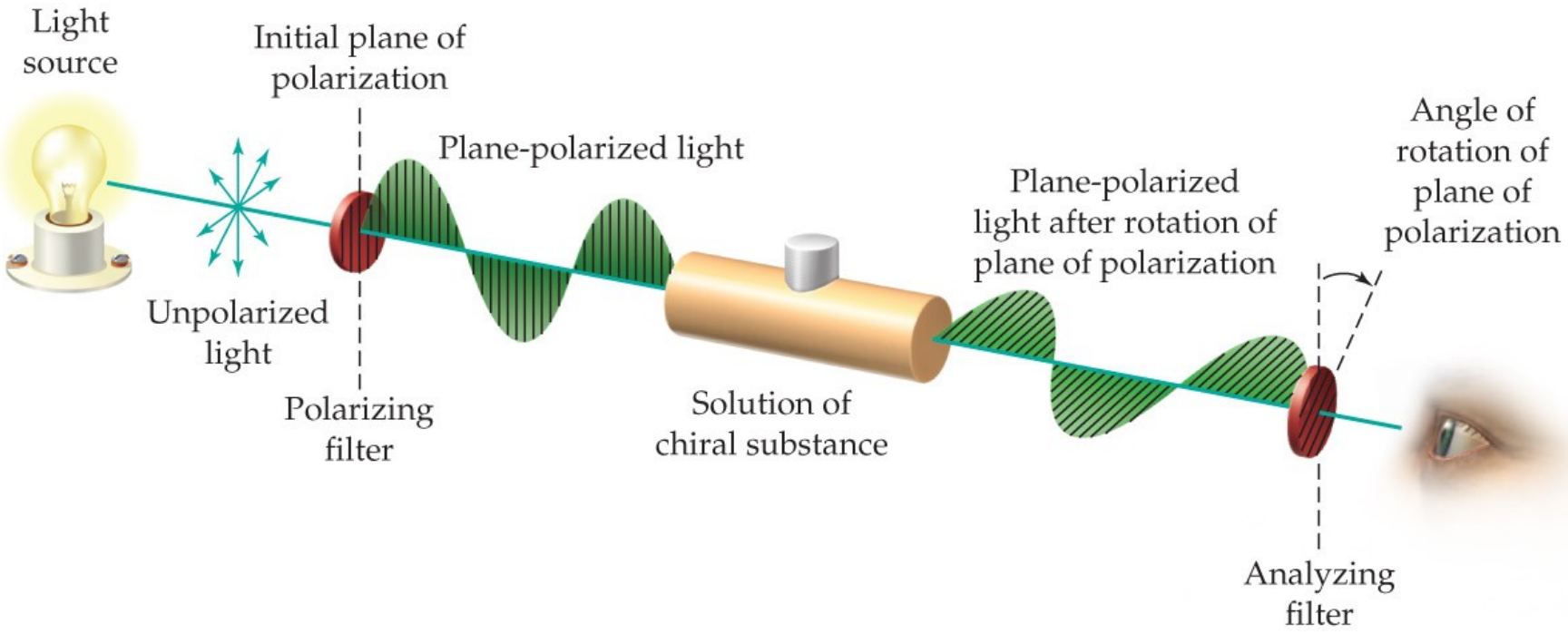


$[Co(en)_3]^{3+}$ has a helical structure in which the three en ligands lie along the threads of a screw. As the red arrows show, one enantiomer is "right-handed" in the sense that the screw would advance into the page as you rotated it to the right (clockwise). The other enantiomer is "left-handed" because it would advance into the page as you rotated it to the left (counterclockwise).



$[Co(NH_3)_6]^{3+}$ has several symmetry planes and is achiral. (Only one of the symmetry planes is identified.)

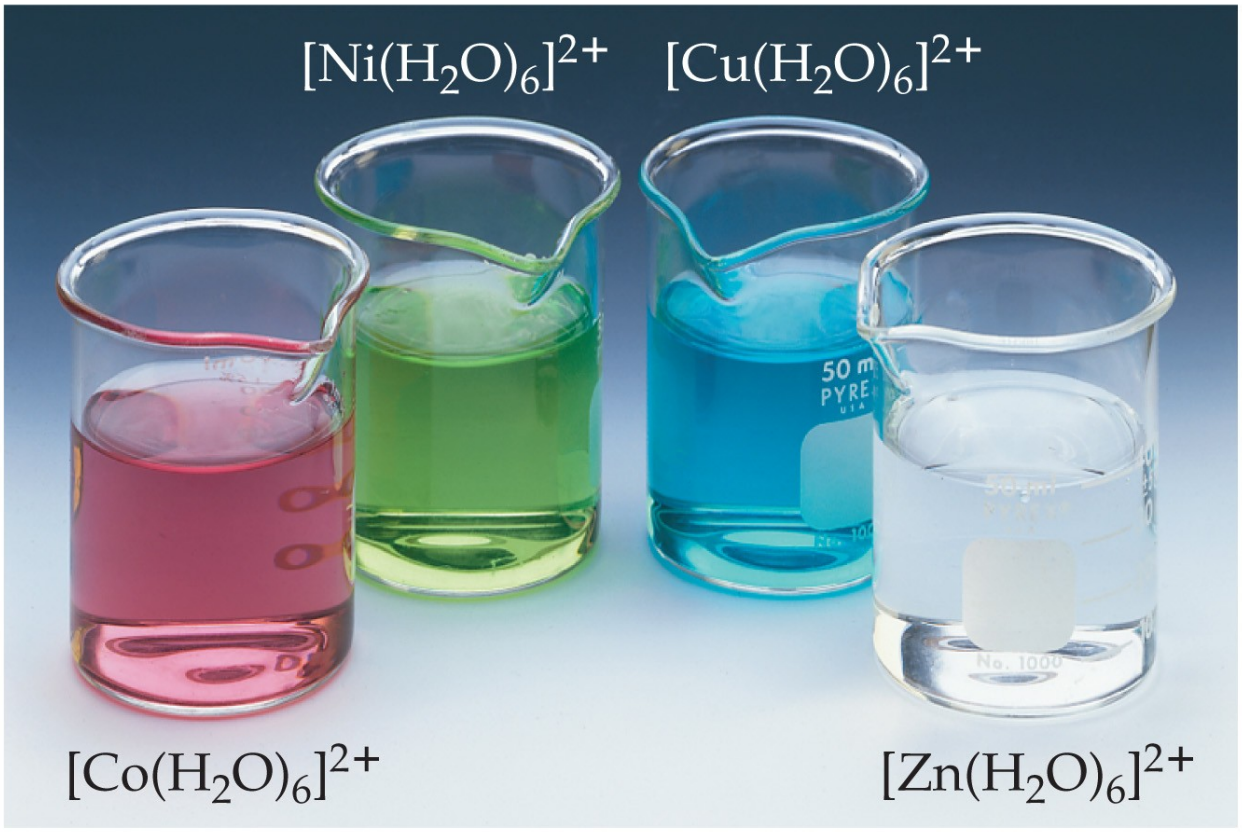
Enantiomers and Molecular Handedness



Color of Transition Metal Complexes

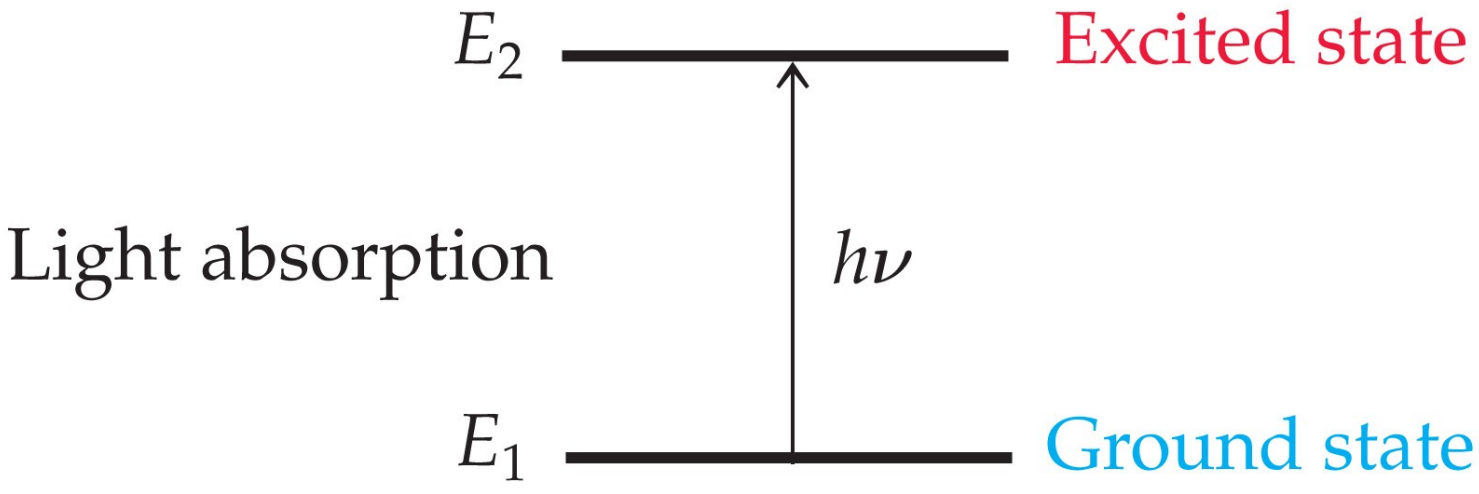
The same metal, but different ligands

Color of Transition Metal Complexes



Different metals, but the same ligand

Color of Transition Metal Complexes



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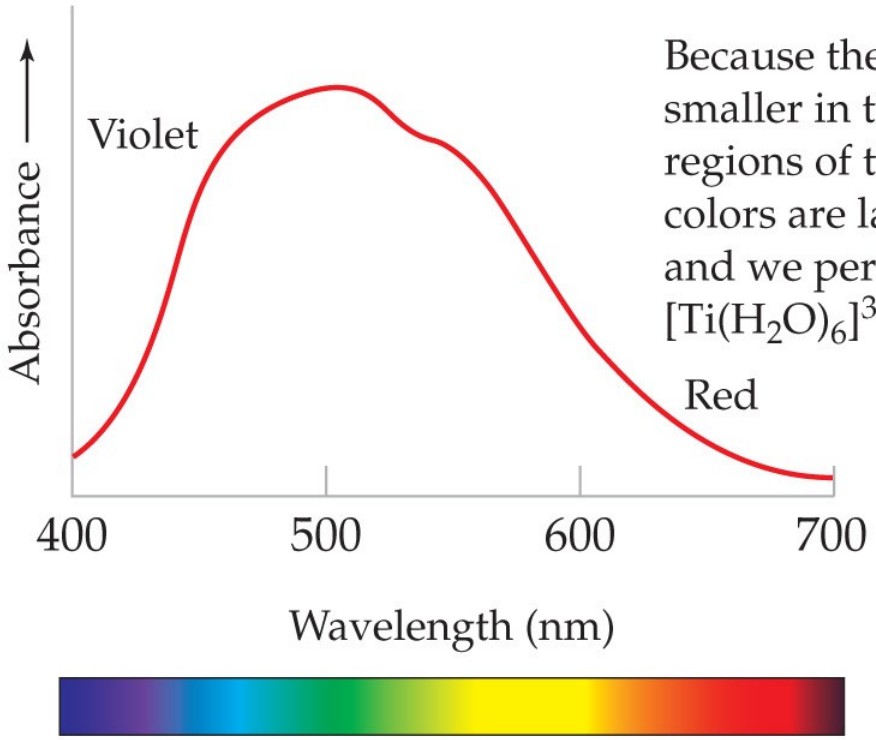
$$\Delta E = E_2 - E_1 = h\nu = \frac{hc}{\lambda}$$

or

$$\lambda = \frac{hc}{\Delta E}$$

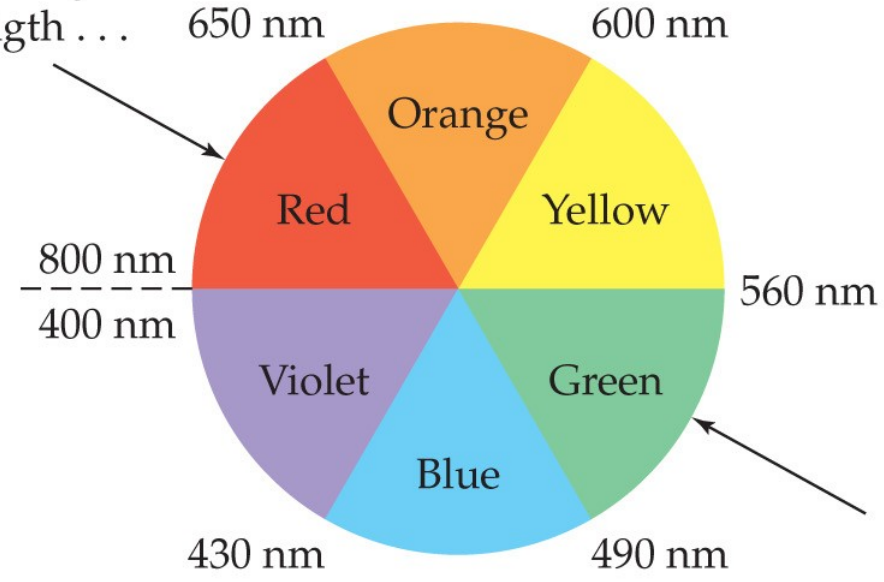
Color of Transition Metal Complexes



Because the absorbance is smaller in the red and violet regions of the spectrum, these colors are largely transmitted and we perceive the color of $[Ti(H_2O)_6]^{3+}$ to be red-violet.

Color of Transition Metal Complexes

Observed and absorbed colors are generally complementary. Thus, if a substance absorbs only red light of 720 nm wavelength . . .



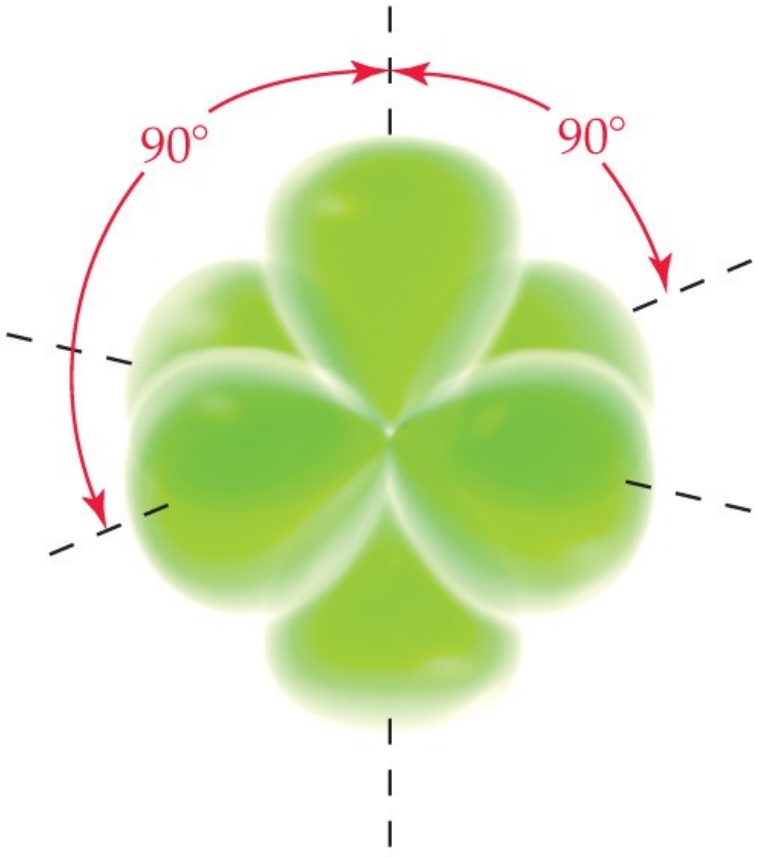
Bonding in Complexes: Valence Bond Theory

Vacant metal hybrid atomic orbital

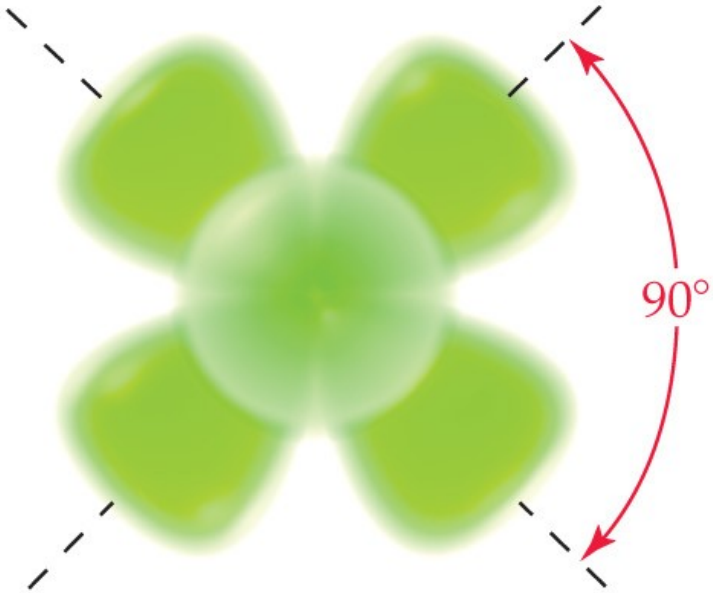
Occupied ligand atomic orbital

Coordinate covalent bond

Bonding in Complexes: Valence Bond Theory



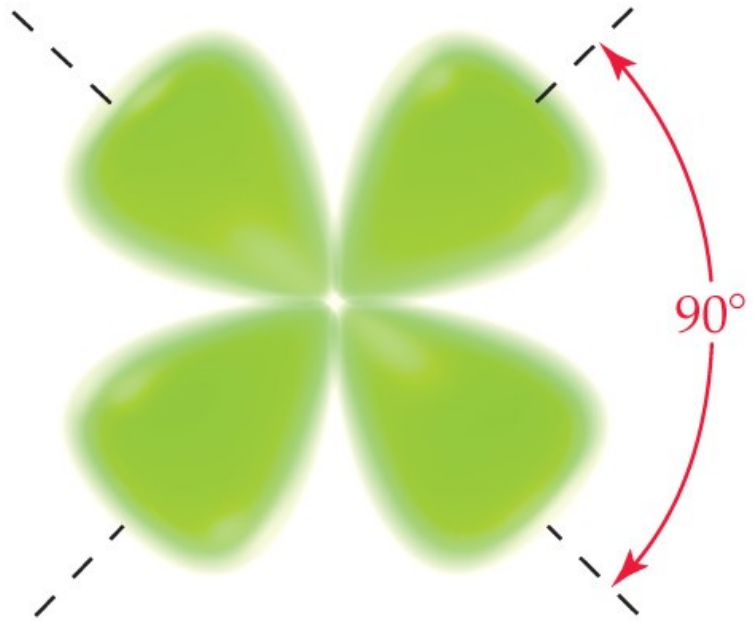
Side view



Top view

Bonding in Complexes: Valence Bond Theory

Side view



Top view

Bonding in Complexes: Valence Bond Theory

TABLE 20.7 Hybrid Orbitals for Common Coordination Geometries

Coordination Number	Geometry	Hybrid Orbitals	Example
2	Linear	sp	$[Ag(NH_3)_2]^+$
4	Tetrahedral	sp^3	$[CoCl_4]^{2-}$
4	Square planar	dsp^2	$[Ni(CN)_4]^{2-}$
6	Octahedral	d^2sp^3 or sp^3d^2	$[Cr(H_2O)_6]^{3+}$, $[Co(H_2O)_6]^{2+}$

Co^{2+}: [Ar] ⇅ ⇅ ↑ ↑ ↑ ___ ___ ___ ___

3*d* 4*s* 4*p*

$[CoCl_4]^{2-}$: [Ar] ⇅ ⇅ ↑ ↑ ↑ ⇅ ⇅ ⇅ ⇅

3*d* 4*s* 4*p*

Four sp^3 bonds to the ligands

Bonding in Complexes: Valence Bond Theory

TABLE 20.7 Hybrid Orbitals for Common Coordination Geometries

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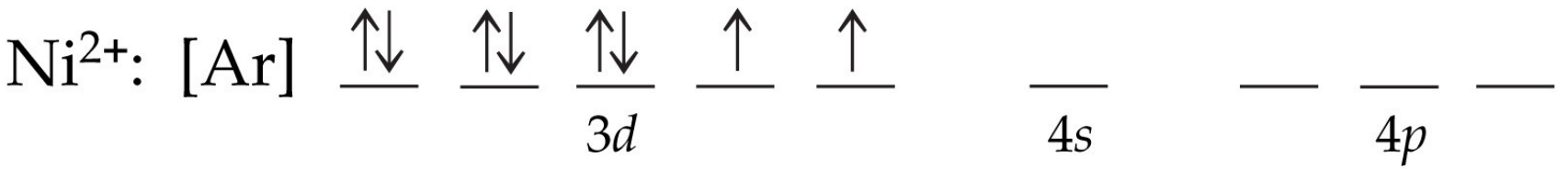
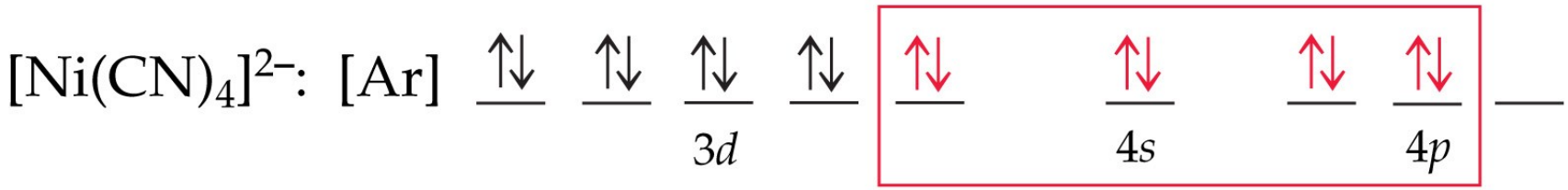
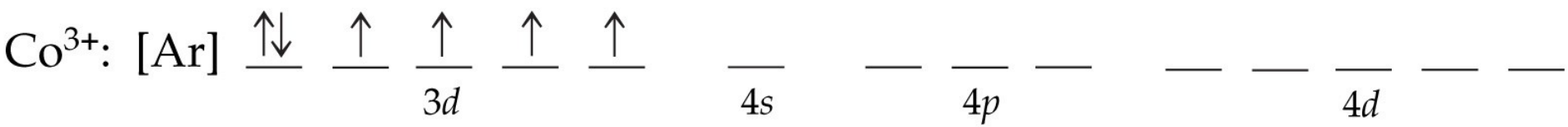
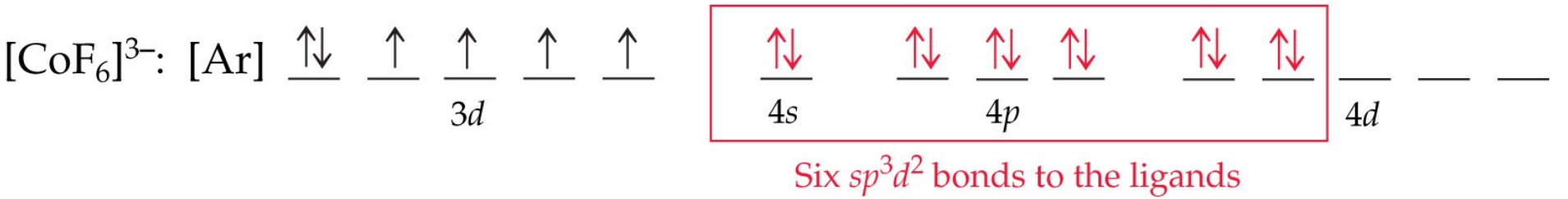




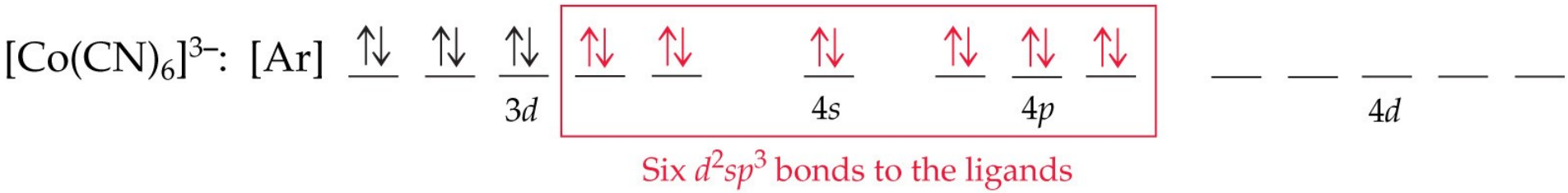
Four dsp^2 bonds to the ligands

Bonding in Complexes: Valence Bond Theory





High spin



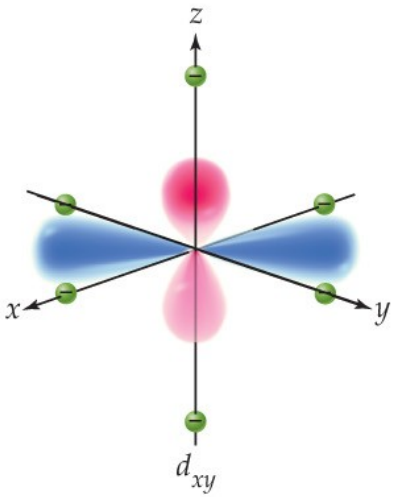
Low spin

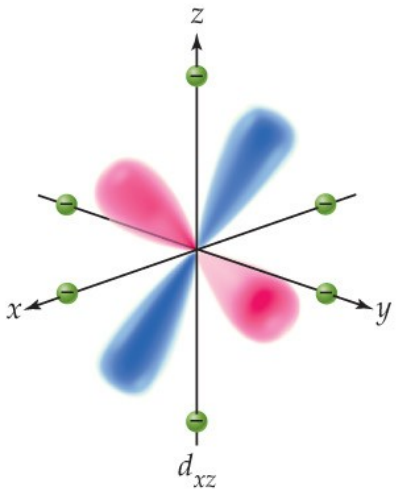
Crystal Field Theory

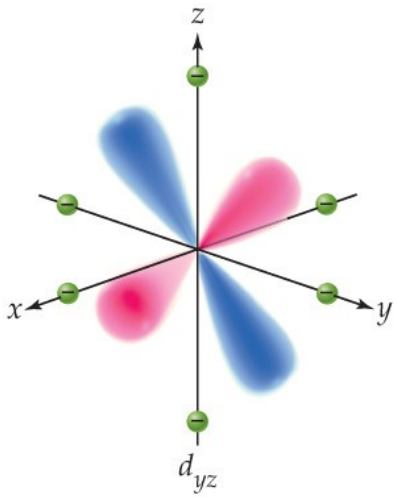
Crystal Field Theory: A model that views the bonding in complexes as arising from electrostatic interactions and considers the effect of the ligand charges on the energies of the metal ion *d* orbitals.

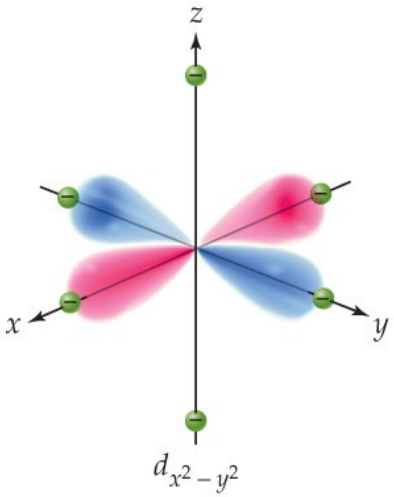
Crystal Field Theory

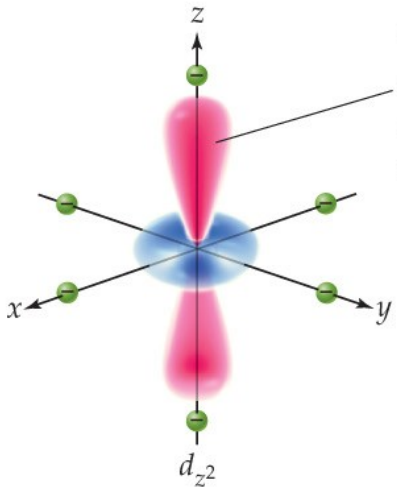
Octahedral Complexes







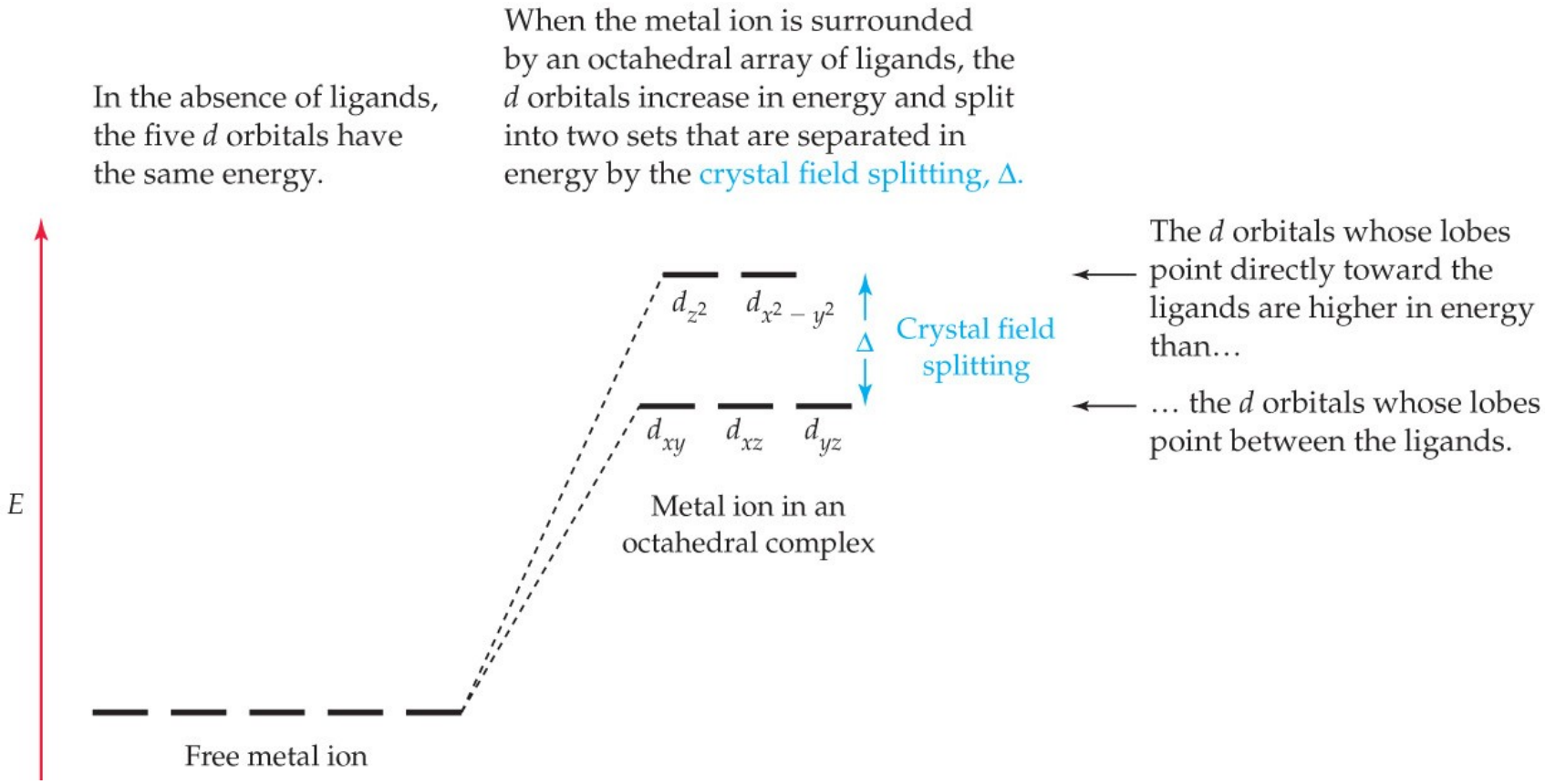




The lobes of the orbitals indicate the regions of space where a *d* electron is most likely to be found.

Crystal Field Theory

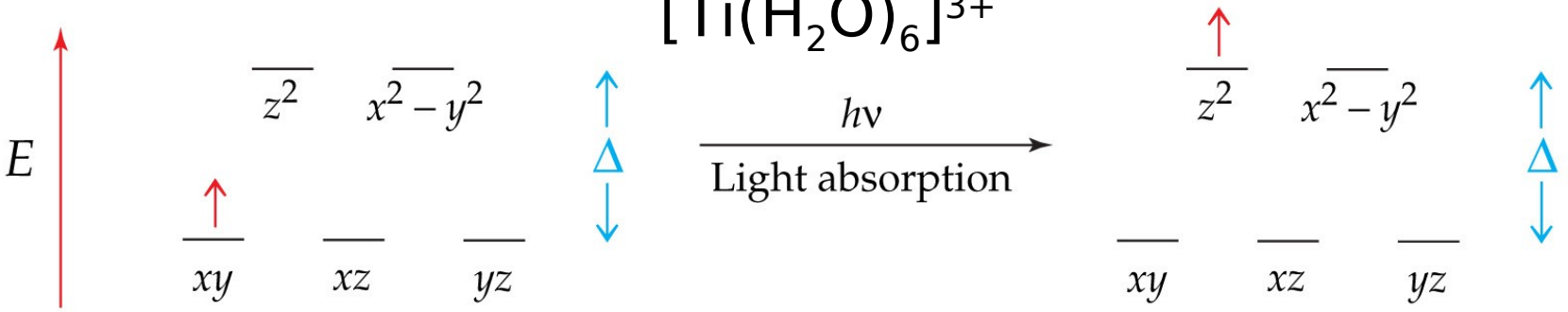
Octahedral Complexes


In the absence of ligands, the five d orbitals have the same energy.
When the metal ion is surrounded by an octahedral array of ligands, the d orbitals increase in energy and split into two sets that are separated in energy by the crystal field splitting, Δ.
E
d_{z^2}
$d_{x^2-y^2}$
Δ
Crystal field splitting
d_{xy}
d_{xz}
d_{yz}
Metal ion in an octahedral complex
Free metal ion
The d orbitals whose lobes point directly toward the ligands are higher in energy than…
… the d orbitals whose lobes point between the ligands.

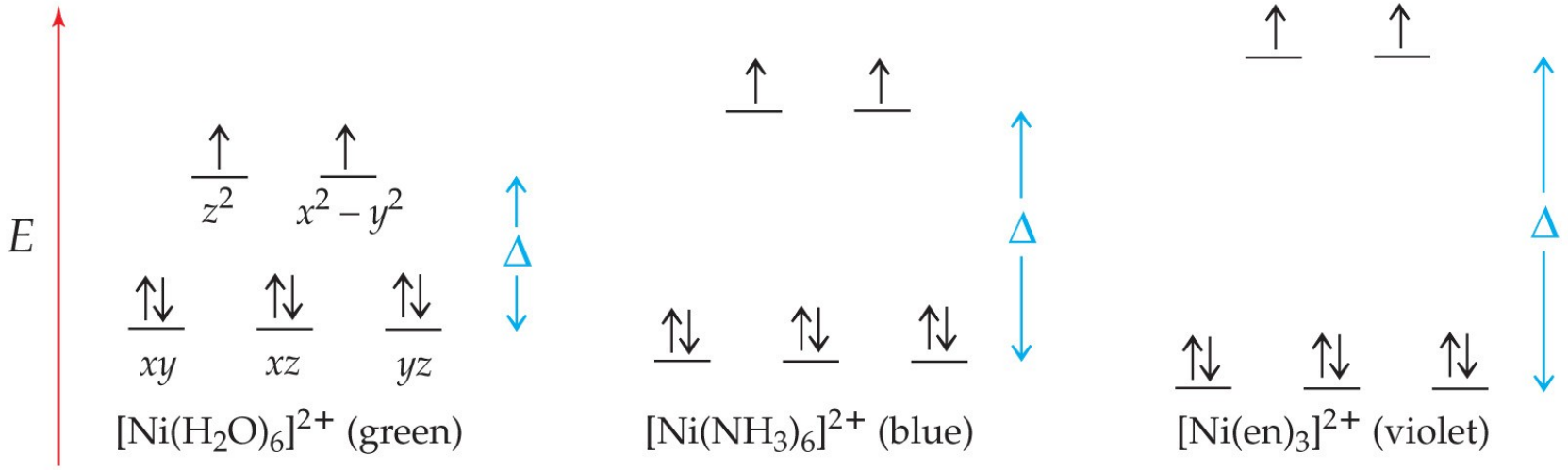
Crystal Field Theory

Octahedral Complexes

$[Ti(H_2O)_6]^{3+}$



$[Ni(X)_6]^{2+}$ X=H_2O, NH_3, and ethylenediamine (en)



Crystal Field Theory

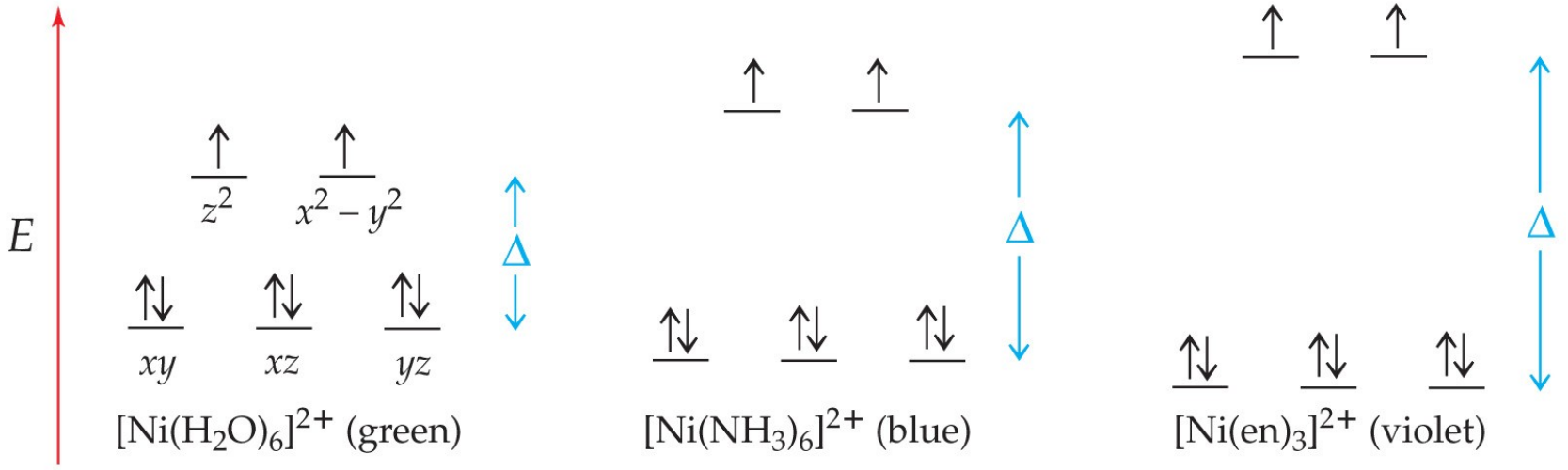
Octahedral Complexes

The crystal field splitting changes according to the spectrochemical series.

Weak-field ligands $I^- < Br^- < Cl^- < F^- < H_2O < NH_3 < en < CN^-$ Strong-field ligands

Increasing Δ

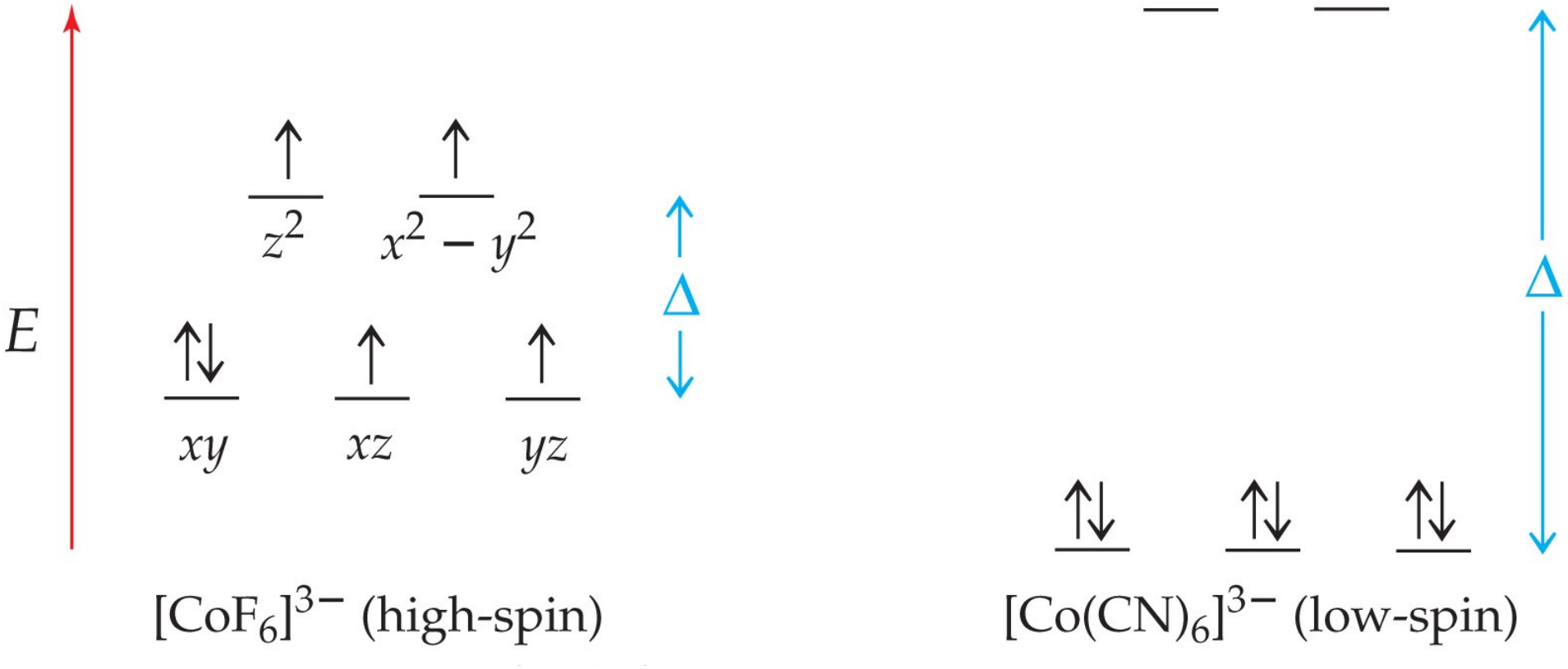
$[Ni(X)_6]^{2+}$ X=H_2O, NH_3, and ethylenediamine (en)



Crystal Field Theory

Octahedral Complexes

This accounts for the magnetic properties of complexes.



Crystal Field Theory

Tetrahedral and Square Planar Complexes